

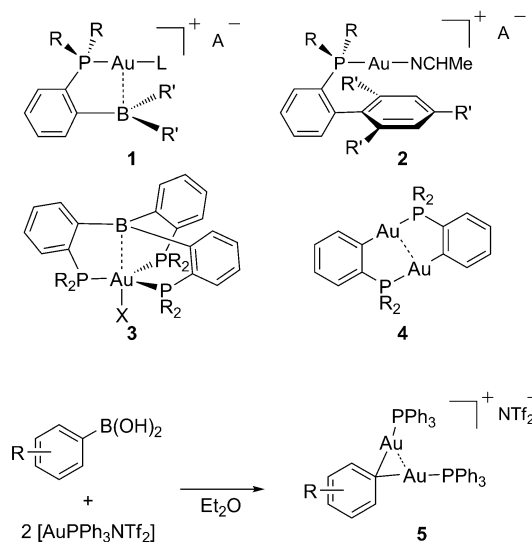
Gold Clusters**A Hexanuclear Gold Cluster Supported by Three-Center–Two-Electron Bonds and Auophilic Interactions****

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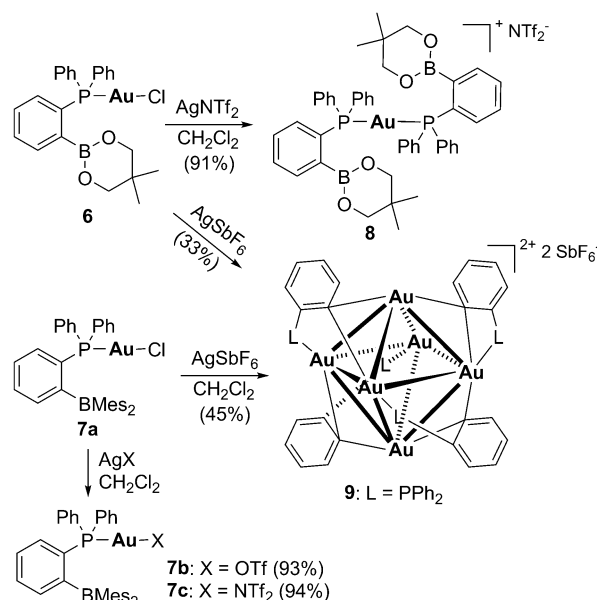
Gold clusters or nanoparticles have been proposed as catalytically active species in a variety of homogeneous processes,^[1–5] which might proceed by mechanisms that are very different from those occurring under homogeneous conditions.^[6,7] The preparation of new types of small gold clusters has attracted recent attention because of their structural novelty and potential for the discovery of new reaction types.^[8] Herein we report the ready preparation of a robust hexagold cluster composed exclusively by Au^I centers that is catalytically active in the activation of alkynes.^[9]

We decided to synthesize new gold(I) complexes of type **1** in which the *ortho*-boryl group could enhance the electrophilicity of the metal center in the catalytic activation of alkynes, allenes, and alkenes. This catalyst design was inspired both by the high reactivity displayed by cationic catalysts of type **2** with sterically hindered Buchwald phosphines^[10] and by the stability of gold(I) boratranes, such as **3** developed by Bourissou, that display significant donor–acceptor Au→B interactions.^[11]

Complexes of type **1** could undergo bimolecular Au^I/B transmetalation to form known dinuclear complexes of type **4**.^[12] Indeed, the reaction of [LAuX] with arylboronic acids leads to aryl gold(I) derivatives [ArAuL] in a general manner,^[13,14] while by using two equivalents of [Ph₃PAuNTf₂], diaurated complexes [(μ-aryl)(Ph₃PAu)₂]NTf₂ (**5**) are obtained (Scheme 1).^[15] Very similar *gem*-diaurated complexes have been obtained by reaction of arylboronic acids with two equivalents of [(Au(IPr))₂(μ-OH)][BF₄].^[16]

**Scheme 1.** Formation of diaurated complexes **5**.

Complexes **6** and **7a** (Scheme 2) were easily prepared in 90–92% yield by reaction of the corresponding *o*-borylphosphines^[17] with [Au(tht)Cl] (tht = tetrahydrothiophene). Inter-

**Scheme 2****Scheme 2.** Formation of hexanuclear gold cluster **9**.

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estingly, whereas reaction of **7a** with AgOTf or AgNTf₂ led to neutral complexes **7b** or **7c** by chloride ligand exchange, **6** reacted with AgNTf₂ to give cationic [AuL₂]⁺Tf₂N[−] complex **8**. Very weak Au→B interactions are present in the solid structure of **7a–c**^[18] (3.55–3.62 Å), which are in the range corresponding to the sum of their van der Waals radii (3.58 Å), whereas in the case of **6** and **8** no interaction was observed in the solid state (Figure 1).

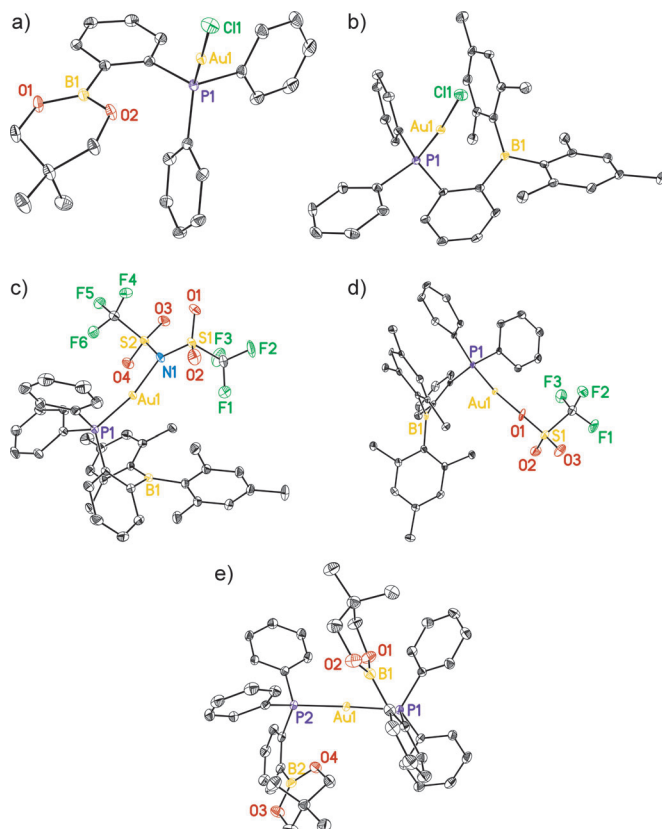


Figure 1. Structure of complexes **6** (a), **7a** (b), **7b** (c), **7c** (d), and **8** (e). ORTEP plot (ellipsoids set at 50% probability). Hydrogen atoms, solvate molecules, and the Tf₂N[−] anion for **8** are omitted for clarity.

In an attempt at preparing a cationic Au^I complex of type **2**, neutral complexes **6** and **7a** were treated with AgSbF₆ at 23 °C in the presence of acetonitrile, benzonitrile, or 2,4,6-trimethoxybenzonitrile. Surprisingly, hexanuclear cluster [AuL₄](SbF₆)₂ **9** was obtained instead as a yellow solid. The best yield (45%) was achieved by treatment of **7a** with AgSbF₆ in CH₂Cl₂ at 23 °C. An analogous hexanuclear cluster **9'** was obtained using AgBF₄.

The X-ray crystal structure of the dicationic hexanuclear cluster **9** shows a pseudooctahedral geometry with two types of gold atoms: four Au^I centers (Au1, Au2, Au4, and Au6) bonded to the carbon and phosphorous atoms of the L ligands and two Au^I centers (Au3 and Au5) bonded to carbon atoms through three-center–two-electron bonds (Figure 2). Owing to the distortion of planarity formed by the four gold atoms, the cluster is C_{2v}-symmetric instead of D_{4h}-symmetric. Dicationic hexanuclear clusters [Au₆(PR₃)₆]²⁺(A[−])₂ have distorted

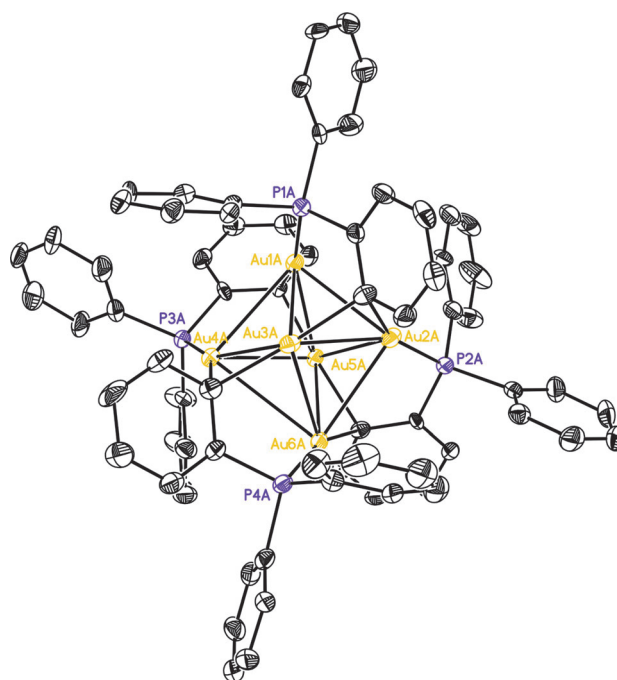


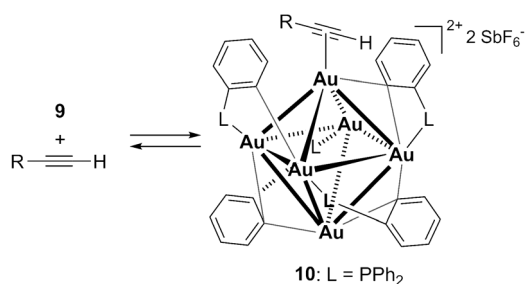
Figure 2. Structure of dicationic [Au₆]²⁺ cluster **9**. ORTEP plot (ellipsoids set at 50% probability). Hydrogen atoms, SbF₆[−] anions, and solvate molecules are omitted for clarity.

octahedral^[19] or edge-sharing bitetrahedral structures^[20] with average Au–Au bond distances of 3.02 Å and 2.76 Å, respectively. In cluster **9**, the average Au–Au bond length is 3.05 Å, with a closest Au⋯Au interaction of 2.71 Å, which is the shortest bond distance between gold atoms in structurally characterized hexanuclear gold clusters. This distance is within the range observed for homoleptic mesitylgold complex (AuMes)₆ (2.69–2.71 Å) with a five-pointed star structure.^[21]

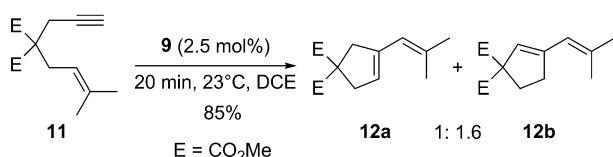
Cluster **9** is unique among hexanuclear gold clusters as it bears only four phosphines to stabilize six Au^I centers and features four *ipso*-carbon–digold interactions.^[22] In contrast to the carbon-centered hexagold cluster [CAu₆(dppy)₆](BF₄)₂ (dppy = diphenylphosphino-2-pyridine), which is non-emissive in solution,^[23] complex **9** shows emission at room temperature in CH₂Cl₂ solution with the maximum at circa 460 nm that is due to an intraligand and/or metal-to-ligand transitions. In the solid state, **9** displays more intense emission, which is substantially red-shifted with the maximum at ca. 550 nm.

Although **9** is quite robust and does not react at 23 °C with nitriles, isonitriles, or pyridine, it is conceivable that the two gold atoms Au3 and Au5 bonded to the *ortho* carbons of the aryl phosphines by relatively weak three-center–two-electron bonds could act as electrophilic centers to activate alkynes by complexes **10** (Scheme 3).

Accordingly, treatment of 1,6-enyne **11** with gold cluster **9** as the catalyst led to dienes **12a,b**^[24] (Scheme 4). Cluster **9** was quantitatively recovered from the reaction mixture. Furthermore, no induction period was observed by monitoring the cycloisomerization of **11a** to **12a,b** in CD₂Cl₂ at 0–23 °C.^[25]



Scheme 3. Formation of alkyne adduct **10**.

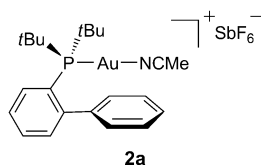


Scheme 4. Formation of **12a** and **12b**. DCE = 1,2-dichloroethane.

Catalyst **7c** with a NTf₂ ligand is a more reactive catalyst than **9**. The more demanding [4+2] cycloaddition^[10a,26] of 1,6-enyne **13** bearing a disubstituted alkyne with a *o*-tolyl substituent (Table 1). For this cycloisomerization, catalyst

Table 1: [4+2] Cycloaddition of enyne **13** to form **14**.

Entry	Catalyst	t [h]	Yield [%]
1	9	12	73
2	7c	0.75	71
3	2a	1.5	77



7c (entry 2) was found to be even more active for the formation **14** than cationic complex **2a** with JohnPhos ligand.

In summary, we have prepared a robust hexanuclear (Au^I)₆ cluster **9** with two of the Au^I centers bound only to two carbons and four other Au^I centers by three-center-two-electron bonds. This gold cluster is catalytically active in a variety of gold-catalyzed reactions. We have also found that complex **7c** with a borylphosphine ligand is catalyst more reactive than [(2-biphenyl)tBu₂P)Au(MeCN)]SbF₆ (**2a**) in a more challenging cycloisomerization reaction. Synthesis of new gold complexes based on these motifs and further mechanistic studies to determine the reactivity of cluster **9** are underway.

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- [1] a) M. Stratakis, H. García, *Chem. Rev.* **2012**, *112*, 4469–4506; b) J. Han, Y. Liu, R. Guo, *J. Am. Chem. Soc.* **2009**, *131*, 2060–2061; c) G. Kyriakou, S. K. Beaumont, S. M. Humphrey, C. Antonetti, R. M. Lambert, *ChemCatChem* **2010**, *2*, 1444–1449; d) V. K. Kanuru, G. Kyriakou, S. K. Beaumont, A. C. Papageorgiou, D. J. Watson, R. M. Lambert, *J. Am. Chem. Soc.* **2010**, *132*, 8081–8086; e) S. K. Beaumont, G. Kyriakou, R. M. Lambert, *J. Am. Chem. Soc.* **2010**, *132*, 12246–12248; f) A. Corma, R. Juárez, M. Boronat, F. Sánchez, M. Iglesias, H. García, *Chem. Commun.* **2011**, 47, 1446–1448.
- [2] M. Comotti, C. Della Pina, R. Matarrese, M. Rossi, *Angew. Chem.* **2004**, *116*, 5936–5939; *Angew. Chem. Int. Ed.* **2004**, *43*, 5812–5815.
- [3] a) P. S. D. Robinson, G. N. Khairallah, G. da Silva, H. Lioe, R. A. J. O'Hair, *Angew. Chem.* **2012**, *124*, 3878–3883; *Angew. Chem. Int. Ed.* **2012**, *51*, 3812–3817; b) A. S. K. Hashmi, *Science* **2012**, *338*, 1434–1434.
- [4] J. Oliver-Meseguer, J. R. Cabrero-Antonino, I. Dominguez, A. Leyva-Perez, A. Corma, *Science* **2012**, *338*, 1452–1455.
- [5] G. Li, R. Jin, *Acc. Chem. Res.* **2013**, DOI: 10.1021/ar300213z.
- [6] M. García-Mota, N. Cabello, F. Maseras, A. M. Echavarren, J. Pérez-Ramírez, N. López, *ChemPhysChem* **2008**, *9*, 1624–1629.
- [7] C. Gryparis, C. Efe, C. Raptis, I. N. Lykakis, M. Stratakis, *Org. Lett.* **2012**, *14*, 2956–2959.
- [8] a) T. J. Robilotto, J. Bacsa, T. G. Gray, J. P. Sadighi, *Angew. Chem.* **2012**, *124*, 12243–12246; *Angew. Chem. Int. Ed.* **2012**, *51*, 12077–12080; b) E. S. Borren, A. F. Hill, R. Shang, M. Sharma, A. C. Willis, *J. Am. Chem. Soc.* **2013**, *135*, 4942–4945; c) X.-L. Pei, Y. Yang, Z. Lei, Q.-M. Wang, *J. Am. Chem. Soc.* **2013**, *135*, 6435–6437.
- [9] a) A. S. K. Hashmi, *Chem. Rev.* **2007**, *107*, 3180–3211; b) E. Jiménez-Núñez, A. M. Echavarren, *Chem. Commun.* **2007**, 333–346; c) D. J. Gorin, B. D. Sherry, F. D. Toste, *Chem. Rev.* **2008**, *108*, 3351–3378; d) A. S. K. Hashmi, M. Rudolph, *Chem. Soc. Rev.* **2008**, *37*, 1766–1775; e) Z. Li, C. Brouwer, C. He, *Chem. Rev.* **2008**, *108*, 3239–3265; f) E. Jiménez-Núñez, A. M. Echavarren, *Chem. Rev.* **2008**, *108*, 3326–3350; g) V. Michelet, P. Y. Toullec, J. P. Genêt, *Angew. Chem.* **2008**, *120*, 4338–4386; *Angew. Chem. Int. Ed.* **2008**, *47*, 4268–4315; h) M. Rudolph, A. S. K. Hashmi, *Chem. Soc. Rev.* **2012**, *41*, 2448–2462.
- [10] a) C. Nieto-Oberhuber, S. López, A. M. Echavarren, *J. Am. Chem. Soc.* **2005**, *127*, 6178–6179; b) E. Herrero-Gómez, C. Nieto-Oberhuber, S. López, J. Benet-Buchholz, A. M. Echavarren, *Angew. Chem.* **2006**, *118*, 5581–5585; *Angew. Chem. Int. Ed.* **2006**, *45*, 5455–5459; c) P. Pérez-Galán, N. Delpont, E. Herrero-Gómez, F. Maseras, A. M. Echavarren, *Chem. Eur. J.* **2010**, *16*, 5324–5332.
- [11] a) S. Bontemps, G. Bouhadir, W. Gu, M. Mercy, C.-H. Chen, B. M. Foxman, L. Maron, O. V. Ozerov, D. Bourissou, *Angew. Chem.* **2008**, *120*, 1503–1506; *Angew. Chem. Int. Ed.* **2008**, *47*, 1481–1484; b) M. Sircoglou, S. Bontemps, G. Bouhadir, N. Saffon, K. Miqueu, W. Gu, M. Mercy, C.-H. Chen, B. M. Foxman, L. Maron, O. V. Ozerov, D. Bourissou, *J. Am. Chem. Soc.* **2008**, *130*, 16729–16738; c) for the In^{III} analogue of **3**, see: E. J. Derrah, M. Sircoglou, M. Mercy, S. Ladeira, G. Bouhadir, K. Miqueu, L. Maron, D. Bourissou, *Organometallics* **2011**, *30*, 657–660.
- [12] a) M. A. Bennett, S. K. Bhargava, K. D. Griffiths, G. B. Robertson, W. A. Wickramasinghe, A. C. Willis, *Angew. Chem.* **1987**,

- 99, 261–262; *Angew. Chem. Int. Ed. Engl.* **1987**, 26, 258–260; b) M. A. Bennett, S. K. Bhargava, N. Mirzadeh, S. H. Privér, J. Wagler, A. C. Willis, *Dalton Trans.* **2009**, 7537–7551; c) T.-P. Lin, I.-S. Ke, F. P. Gabbaï, *Angew. Chem.* **2012**, 124, 5069–5072; *Angew. Chem. Int. Ed.* **2012**, 51, 4985–4988.
- [13] a) D. V. Partyka, M. Zeller, A. G. Hunter, T. G. Gray, *Angew. Chem.* **2006**, 118, 8368–8371; *Angew. Chem. Int. Ed.* **2006**, 45, 8188–8191; b) D. V. Partyka, J. B. Updegraff, M. Zeller, A. D. Hunter, T. G. Gray, *Organometallics* **2009**, 28, 1666–1674; c) L. Gao, M. A. Peay, D. V. Partyka, J. B. Updegraff, T. S. Teets, A. J. Esswein, M. Zeller, A. D. Hunter, T. G. Gray, *Organometallics* **2009**, 28, 5669–5681; d) D. V. Partyka, T. S. Teets, M. Zeller, J. B. Updegraff, A. D. Hunter, T. G. Gray, *Chem. Eur. J.* **2012**, 18, 2100–2112; e) M. A. Peay, J. E. Heckler, N. Deligonul, T. G. Gray, *Organometallics* **2011**, 30, 5071–5074; f) D. V. Partyka, M. Zeller, A. D. Hunter, T. G. Gray, *Inorg. Chem.* **2012**, 51, 8394–8401.
- [14] A. S. K. Hashmi, T. D. Ramamurthi, F. Rominger, *J. Organomet. Chem.* **2010**, 694, 592–597.
- [15] J. E. Heckler, M. Zeller, A. D. Hunter, T. G. Gray, *Angew. Chem.* **2012**, 124, 6026–6030; *Angew. Chem. Int. Ed.* **2012**, 51, 5924–5928.
- [16] A. Gómez-Suárez, S. Dupuy, A. M. Z. Slawin, S. P. Nolan, *Angew. Chem.* **2013**, 125, 972–976; *Angew. Chem. Int. Ed.* **2013**, 52, 938–942.
- [17] a) S. Porcel, G. Bouhadir, N. Saffon, L. Maron, D. Bourissou, *Angew. Chem.* **2010**, 122, 6322–6325; *Angew. Chem. Int. Ed.* **2010**, 49, 6186–6189; b) T. W. Hudnall, Y.-M. Kim, M. W. P. Bebbington, D. Bourissou, F. P. Gabbaï, *J. Am. Chem. Soc.* **2008**, 130, 10890–10891.
- [18] CCDC 934740 (**7c**), 934741 (**7b**), 934742 (**9**), 934743 (**9'**), 934744 (**7a**), 934745 (**6**), and 934746 (**8**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [19] P. L. Bellon, M. Manaserro, M. Sansoni, *J. Chem. Soc. Dalton Trans.* **1973**, 2423–2427.
- [20] a) C. E. Briant, K. P. Hall, M. P. Mingos, *J. Organomet. Chem.* **1983**, 254, C18–C20; b) C. E. Briant, K. P. Hall, M. P. Mingos, A. C. Wheeler, *J. Chem. Soc. Dalton Trans.* **1986**, 687–692.
- [21] S. Gambarotta, C. Floriani, A. Chiesi-Villa, C. Guastini, *J. Chem. Soc. Chem. Commun.* **1983**, 1304–1306.
- [22] For a pentanuclear cluster $[\text{Au}_5(\text{C}_6\text{H}_4\text{PPh}_2)_4]\text{OTf}$ with two *ipso*-carbon–digold interactions, see: M. A. Bennett, L. L. Welling, A. C. Willis, *Inorg. Chem.* **1997**, 36, 5670–5672.
- [23] J.-H. Jia, J.-X. Liang, Z. Lei, Z.-X. Cao, Q.-M. Wang, *Chem. Commun.* **2011**, 47, 4739–4741.
- [24] a) C. Nieto-Oberhuber, M. P. Muñoz, E. Buñuel, C. Nevado, D. J. Cárdenas, A. M. Echavarren, *Angew. Chem.* **2004**, 116, 2456–2460; *Angew. Chem. Int. Ed.* **2004**, 43, 2402–2406; b) C. Nieto-Oberhuber, M. P. Muñoz, S. López, E. Jiménez-Núñez, C. Nevado, E. Herrero-Gómez, M. Raducan, A. M. Echavarren, *Chem. Eur. J.* **2006**, 12, 1677–1693.
- [25] See the Supporting Information for further experiments.
- [26] a) C. Nieto-Oberhuber, P. Pérez-Galán, E. Herrero-Gómez, T. Lauterbach, C. Rodríguez, S. López, C. Bour, A. Rosellón, D. J. Cárdenas, A. M. Echavarren, *J. Am. Chem. Soc.* **2008**, 130, 269–279.